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(19) (CA) **CANADIAN PATENT** (12)

(54) PREPARATION OF OLEFINS FROM CRUDE METHANOL

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Preparation of olefins from crude methanol

Recently, endeavors to use methanol for the preparation of olefins have aroused increasing interest.

Methanol can easily be prepared from coal by means of well-established technologies, via coal gasification and the preparation of synthesis gas. Should it prove possible to convert methanol economically to lower olefins, the further conversion processes which are at present conventionally used in the chemical industry could be retained if coal was used as the raw material. Hence, processes have been developed

10 in recent years for preparing olefins from methanol and/or dimethyl ether. Such a process is described, for example, in German Laid-Open Application DOS 2,615,150 published on October 21, 1976. The catalyst used in this process is the aluminosilicate zeolite ZSM-5, which in fact is a catalyst for aromatization reactions. However, the reaction can be directed towards the formation of olefins by taking various measures, in particular by reducing the residence time. Other measures which favor olefin formation are the dilution of methanol or of dimethyl ether with inert gases,

20 or the dilution of the catalyst with binders. Experience shows that high olefin yields can only be achieved if the methanol and/or dimethyl ether is very greatly diluted with inert gases. Hence, the process is uneconomical. Other processes which have been disclosed have the disadvantage that the catalyst throughput is low, and that the catalyst carbonizes rapidly. There is therefore

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great interest in a simple process which permits complete conversion of crude methanol and/or dimethyl ether into hydrocarbons consisting in the main of C<sub>2</sub>-C<sub>5</sub>-olefins.

We have found that C<sub>2</sub>-C<sub>5</sub>-olefins are obtained in a simple manner from crude methanol and/or dimethyl ether by catalytic conversion at an elevated temperature in the presence of a zeolite-containing catalyst, if the zeolite has been prepared from technical-grade waterglass with the aid of hexamethylenediamine, without addition of a metal salt.

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In a preferred embodiment, crude methanol is reacted over the zeolite catalyst according to the invention at between atmospheric pressure and about 30 bar, and at from 300 to 700°C, preferably from 400 to 650°C. Crude methanol for the purposes of the invention means methanol containing up to about 30% by weight of water, i.e. the product formed in the synthesis of methanol. Other lower alcohols may also be present in the crude methanol. The catalyst throughput, expressed in g of methanol and/or dimethyl ether/g of catalyst.h is advantageously selected to be such that the latter compounds are converted as completely as possible, thereby eliminating separation and recycling problems. In general, therefore, the throughput is of the order of from 2 to 50, preferably from 5 to 15, g/g of zeolite.h. However, it is possible to select higher throughputs, or to dilute the starting materials with an inert gas, for example nitrogen, without adverse effect on the composition of the hydrocarbon mixture formed. At the same time it is

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a particular advantage of the invention that the conversion of crude methanol or dimethyl ether to C<sub>2</sub>-C<sub>5</sub>-olefins can be carried out without a diluent.

The zeolites described in German Patent Application P 28 31 344.0 published on March 15, 1979 can be used as zeolite catalysts. These catalysts are distinguished by particularly high activity and selectivity.

The example which follows illustrates the invention.

#### EXAMPLE

##### Preparation of the zeolite:

10 Three solutions are prepared. Solution 1 consists of 326.6 g of technical-grade waterglass (containing 8% by weight of Na<sub>2</sub>O and 28% by weight of SiO<sub>2</sub>) and 352 g of water.

Solution 2 consists of 300 g of a 50 per cent strength aqueous hexamethylenediamine solution and solution 3 consists of 508.3 g of water and 24.7 g of 96 per cent strength sulfuric acid. Solutions 2 and 3 are successively added to solution 1, whilst stirring. The resulting solution is heated for 5 days at 150°C under its autogenous pressure in a steel autoclave. The resulting product is 20 filtered off, washed and dried at 100°C.

##### Preparation of the catalyst from the zeolite:

The zeolite obtained is mixed with boehmite in a ratio such that the zeolite content in the mixture is about 65% by weight, based on anhydrous and amine-free product. The mixture is then

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kneaded with water and extruded to form strands of 1 mm diameter. These are calcined at 540°C, then treated with an aqueous ammonium sulfate solution at 80°C, filtered off, washed and dried.

Conversion of crude methanol to olefins:

20 g (dry weight) of this catalyst are introduced into a flow-tube reactor of 20 mm diameter and the activity in respect of the conversion of crude methanol to olefins is tested. The reaction conditions and experimental results are shown in the Table which follows.

10 The reaction products were analyzed by gas chromatography.

Entry temperature	400°C
Temperature rise	200°C
Pressure	1.3 bar
Throughput	170 g of crude methanol/h
Total throughput	1,000 g
Conversion	95-100%

The reaction product obtained has the following composition:

20 Liquid hydrocarbons, 18% by weight, based on CH<sub>2</sub> employed  
Gaseous hydrocarbons, 82% by weight, based on CH<sub>2</sub> employed,  
and containing the following:

Olefins	C <sub>2</sub> 20% by volume
	C <sub>3</sub> 43% " "
	C <sub>4</sub> 16% " "
	C <sub>5</sub> 5% " "
Paraffins	C <sub>1</sub> 4 " "
	C <sub>2</sub> traces
	C <sub>3</sub> 2% by volume
	C <sub>4</sub> 10% " "

We claim:-

1. A process for the preparation of  $C_2$ - $C_5$ -olefins from crude methanol and/or dimethyl ether by catalytic conversion at an elevated temperature in the presence of a zeolite-containing catalyst, wherein the zeolite has been prepared from technical-grade waterglass with the aid of hexamethylenediamine, without addition of a metal salt.
2. A process as claimed in claim 1, wherein undiluted crude methanol and/or dimethyl ether is used as the starting material.